

Non-planar phthalocyanines with Q-bands beyond 800 nm

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Abstract—Free base and zinc 1,4,8,11,15,18,22,25-octa(*p*-methoxyphenyl) phthalocyanine have been synthesized. The Q-bands are located beyond 800 nm due to combined effects of red-shifts caused by ligand deformation and the electron-donating properties of the methoxy substituents. The phthalocyanines reported in this study could potentially replace naphthalocyanines as absorbers in the 800 nm region within practical applications.

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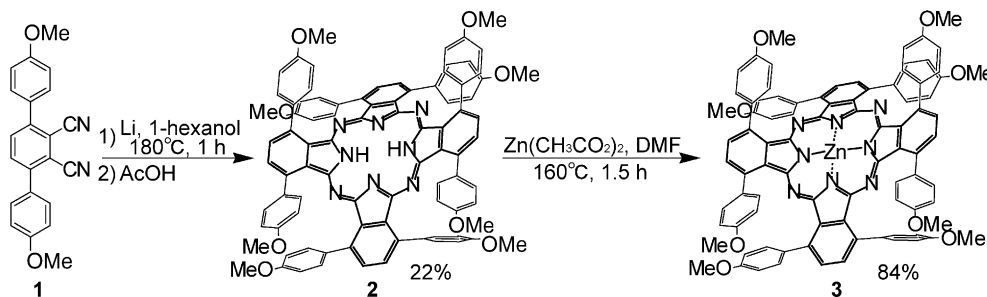
Phthalocyanines (Pcs) are generally blue-green in color due to the intense $\pi \rightarrow \pi^*$ bands associated with the planar heteroaromatic π -conjugation system. As a result, Pcs have been used extensively in dyes and pigments, optical discs, photo-sensitizers, solar cells, and so forth.¹ Most of the applications of Pcs stem from their characteristic π -conjugation systems. Recently, we have synthesized free base and metal complexes of 1,4,8,11,15,18,22,25-octaphenylated Pc (PcPh₈), which show significant deviations from ligand planarity due to the steric congestion of the substituents.² Most metal Pc complexes have extremely planar ligand structures,³ although some large metal ions such as Pb are known to distort the geometry to a minor extent.⁴ Interestingly, the Q-band (the lowest energy spin allowed $\pi \rightarrow \pi^*$ transitions) of PcPh₈ shifts markedly to the red. Our studies have revealed that the Q-band energies of ZnPcPh₈ and of a hypothetical phenyl-removed non-planar ZnPc model complex are almost identical, suggesting that the presence of the phenyl groups has a limited effect on the Q-band energy and that the red-shifts can, therefore, be attributed primarily to ligand deformation.⁵ Recently, near-infrared (NIR) absorbers have attracted considerable attention for use as thermal radiation absorbing materials and in security colorants.⁶ The first synthetic strategy that was used to obtain NIR absorbing Pc derivatives was to enlarge the π -system, since naphthalocyanine (Nc) and anthracocyanine (Ac) exhibit Q-bands at longer wavelengths than Pc.⁷ However,

the stabilities and yields of Ncs and Acs are generally low. Another approach is the introduction of peripheral electron-donating substituents, although there are some drawbacks to this approach.⁸ Fox and Goldberg reported that the insertion of P(V) causes a large red-shift in the Q-band and as a consequence, the Q-band of ionic [(BuO)₈(Pc)P(OCH₃)₂]⁺OH[−] lies at 889 nm in methanol.⁹ In this letter, we have succeeded in synthesizing novel neutral NIR absorbers, **2**, and **3** (Scheme 1), by introducing the electron-donating methoxy group to the PcPh₈ without using harmful heavy metals. As shown below, the Q-band peak appears beyond 800 nm, which is a quite rare in the case of Pcs.¹⁰

The starting material, **1**, was prepared according to procedures reported previously.¹¹ Reaction of **1** with lithium hexyloxide for 1 h at 180 °C resulted in the formation of the lithium complex of 1,4,8,11,15,18,22,25-octa(*p*-methoxyphenyl) phthalocyanine. The crude product was purified on a silica gel column using CHCl₃–MeOH (9:1 v/v), after protonation with acetic acid, and a brown band was collected which was found to contain the desired lithium complex product. After recrystallization from CHCl₃–MeOH, the yield was 22%. The addition of a weak acid was required as a pretreatment step for successful chromatography of the free base product, **2**, while in contrast no additional acid was required for lithium–proton exchange of H₂PcPh₈. This observation appears to be consistent with an increase in the electron density on the Pc ligand due to the electron-donating properties of the *p*-methoxy substituents on the phenyls. It should also be noted that the pyrrole NH ¹H NMR signal for **2** was observed at 3.73 ppm, thus showing the shift anticipated for an

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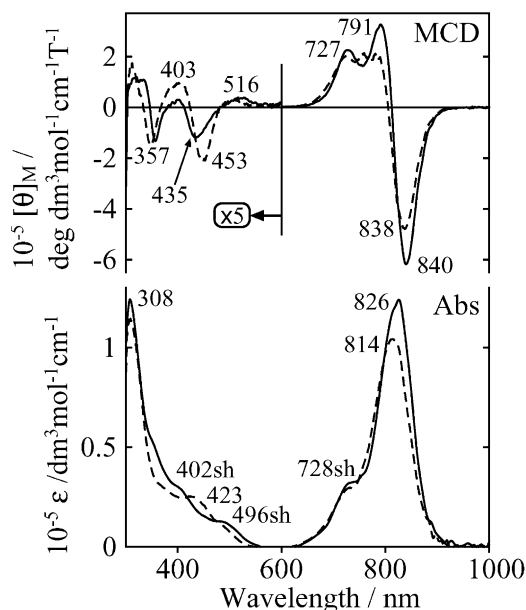
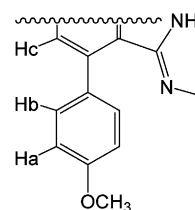
Scheme 1. Synthesis of **2** and **3**.

increase in electron density on the Pc ligand.¹² Compound **2** was then reacted with 20 equiv of anhydrous zinc acetate in DMF to form the zinc complex, **3** (Scheme 1). Insertion of zinc was complete after 90 min. After evaporation of the solvent, the residue was purified using toluene–pyridine (1:1 v/v) on an alumina column in order to avoid possible decomposition of **3** due to the acidity of silica gel. The desired brown solid was obtained in 84% yield. Compounds **2** and **3** were characterized by mass spectrometry, elemental analysis, and ¹H NMR spectroscopy (Scheme 2).^{13,14}

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **2** and **3** in pyridine. Both compounds exhibit an intense, unresolved, Q-band in the NIR region of the absorption spectrum. Despite the reduced symmetry a derivative-shaped Faraday *A*-term type signal appears within the MCD spectrum of **2** at 826 nm. The splitting of states is clearly too small for the component *B*-terms to be resolved so the MCD signal can be regarded as a pseudo *A*-term. The Q-band of the zinc complex, **3**, is blue-shifted relative to that of **2** to 814 nm. In contrast, the Q-bands of unsubstituted H₂Pc (ZnPc) and H₂PcPh₈ (ZnPcPh₈) are located at

694 (672) and 792 (786) nm, respectively, in pyridine.¹⁵ It is clear, therefore, that the introduction of the *p*-methoxy substituents shifts the Q-band significantly to the red. There appears to be no accompanying loss of stability or solubility. The HOMO–LUMO gap is reduced as a result of the destabilization of the HOMO due to the increased electrostatic repulsion between the carbons at 1,4,8,11,15,18,22,25-positions and the electron-rich substituents.^{5,8} Compound **2** showed the first oxidation and reduction couples at –0.10 and –1.40 V (vs ferrocenium/ferrocene) in *o*-dichlorobenzene, respectively, while those of H₂PcPh₈ appeared at –0.01 and –1.39 V, respectively.^{16a} Nc complexes are currently used in practical applications as near-IR absorbers for the 760–820 nm region. Pc complexes should represent an attractive alternative in many instances, since Pc ligands tend to be much more stable. The absorption spectra of **2** and **3** contain several unresolved broad bands in the 300–600 nm region, which, with the exception of a band at 308 nm, are weak relative to the Q-bands. Although the presence of intense absorption bands in the visible region (ca. 400–700 nm) is a prerequisite for use within dyes and pigments,¹⁶ the absence of such bands makes an NIR absorbing complex ideal for security colorant applications. Practically no clear fluorescence emissions were observed for both **2** and **3** in toluene ($\Phi_F < 0.01$). Recent studies on non-planar porphyrins also demonstrated the significantly reduced fluorescence yields compared to their planar analogs.¹⁷

In conclusion, we have reported the synthesis of octa(*p*-methoxyphenyl)-substituted Pcs. The substituent effect of the *p*-methoxyphenyl groups, based on the electron-donating ability of the methoxy groups, clearly shifts the Q-band to the red. As a consequence the Q-band of **2** and **3** lie beyond 800 nm in a region, which is potentially useful for practical applications such as use as

Figure 1. MCD (top) and absorption (bottom) spectra of **2** (solid lines) and **3** (broken lines) in pyridine.Scheme 2. Partial chemical structures of **2** and **3** for the NMR assignments in the footnote.

absorber in security colorants. The synthetic approach reported within this letter should be useful for preparing other novel NIR absorbing materials.

Acknowledgments

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13. Compound **2**: Anal. Calcd for C₈₈H₆₆N₈O₈: C, 77.52; H, 4.88; N, 8.22. Found: C, 76.8; H, 5.0; N, 7.9. MS (ESI) *m/z* 1362 (M⁺). ¹H NMR (pyridine-*d*₅, 400 MHz at 20 °C): δ 7.81 (s, 8H, H_c), 7.76 (d, 16H, H_a), 6.96 (d, 16H, H_b), 3.95 (s, 24H, OCH₃), 3.73 (s, 2H, NH). See [Scheme 2](#) for the proton assignments. UV–vis [λ, nm (log ε)] in pyridine: 826 (5.09), 728sh, 496sh, 402sh, 308 (5.09).
14. Compound **3**: Anal. Calcd for C₈₈H₆₄N₈O₈Zn: C, 74.07; H, 4.52; N, 7.85. Found: C, 73.6; H, 4.6; N, 7.7. MS (ESI) *m/z* 1426 (M⁺). ¹H NMR (pyridine-*d*₅, 400 MHz at 20 °C): δ 7.84 (s, 8H, H_c), 7.81 (d, 16H, H_a), 6.98 (d, 16H, H_b), 3.97 (s, 24H, OCH₃). See [Scheme 2](#) for the proton assignments. UV–vis [λ, nm (log ε)] in pyridine: 814 (5.02), 728sh, 480sh, 423 (4.40), 309 (5.06).
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